Highlights from Recent Literature

1 Analytical

1.1 Crystalline and Electronic Structure of Gold Nanoclusters Determined by EXAFS, XRD and XPS Methods

Gold particle nanoclusters as supported catalysts were analyzed by extended X-ray absorption fine structure, X-ray diffraction, and XPS in order to det. their local, global and electronic structure. N Aldea, P Marginean, V Rednic, S Pintea, B Barz, A Gluhoi, B Nieuwenhuys, Y Xie, F Aldea, M Neumann from the National Institute for Research and Development of Isotopic and Molecular Technologies, Romania. *Journal of Optoelectronics and Advanced Materials* 2007, **9(5)**,1555. The present study points out the strong deformation of the local structure of the active metal due to its interaction with oxide supports as well as a possible oxidation state of the gold component. The average particle size and the microstrain parameters of the supported Au nanoclusters were detected by X-ray diffraction method, based on the Fourier transform of the exptl. X-ray line profiles.

The global structure is obtained with a fitting method using of the generalized Fermi function facilities for the approximation technique. The strong interaction between the metal nanoclusters and oxide supports induces a great change in the local and global microstructures of the catalysts, modifying at the same time the chemisorptions and catalytic processes that occur at the Au-support interface. The following catalyst samples were investigated: Au/ZnO/MgO/Al_2O_3, Au/CuO/Al_2O_3, and Au/Li_2O/CeO_2 Al_2O_3. The XPS technique was used for detecting the electronic states of gold, gold oxide and metal oxides in the oxide supports.

1.2 Support Effects on Electronic Behaviours of Gold Nanoparticles Studied by X-Ray Absorption Fine Structure

The electronic properties of gold nanoparticles supported on different supports were studied with X-ray absorption fine structure (XAFS). Z R Li, W Yan, S Wei from the National Synchrotron Radiation Lab, University of Science and Technology of China, Hefei, 230029, Peop. Rep. China, *AIP Conference Proceedings* 2007, 882(X-Ray Absorption Fine Structure (**XAFS13**), 767 It was found that the tunability of the d-electron distribution in the nano-sized Au clusters can be realized by selective supporting. The Au atoms in the clusters gain 5d electrons when supported on SiO_2, and lose 5d electrons when loaded over MgO, Al_2O_3, and TiO_2. Contractions in bond lengths of between 0.5 and 1.6% from bulk metal values were observedfrom EXAFS data. This work demonstrates that the important role of the different supports in the 5d-charge distribution of Au nanoparticles and usefulness of XAFS in probing the electronic behavior of noble metal nanoparticles.

2 Catalysis

2.1 Kinetics of the Water Formation in the Propene Epoxidation Over Gold-Titania Catalysts

The kinetics of the hydrogen oxidation were detected for a no. of different gold catalysts supported on titania, silica, and silicalite-1. A Nijhuis, B Weckhuysen from the Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven, 5600 MB, Neth. *Preprints - American Chemical Society, Division of Petroleum Chemistry* 2007, **52(2)**, 292. A dual site Langmuir-Hinshelwood kinetic model was able to describe the reaction well. The kinetic parameters are independent of the support. Water was found to be strongly limiting the hydrogen oxidation rate.

2.2 Preparation and Use of Activated Carbon-Supported Gold Catalytic Electrodes for Fuel Cells

This electrode catalyst for a polymer electrolyte fuel cell does not suffer deterioration of catalytic activity due to CO. Preparation Entails the steps of pulverizing and purifying activated C; adding a Au chloride aqueous solution to the activated C to allow Au to be adsorbed to the activated C; and adding an NH_4HCO_3 aqueous solution as a reducing agent. Preferably the content of Au is 5-50% of the activated C and the reducing agent is $NaBH_4$, N_2H_4 or HCOONa. M C Chung, H G Ahn, K P Park, M S Lee, H S Jung, D H Kim, Y J You, J H Lee from the Industry-Academy Cooperation Crops of Sunchon National University, S. Korea. Patent No KR 2007014379 A, January 2007

2.3 Influence of Supporting Materials on Catalytic Activities of Gold Nanoparticles as CO-Tolerant Catalysts in DMFC

Au nanoparticles supported on Pt-Sn/C and Pt/C (nano-Au/Pt-Sn/C and nano-Au/Pt/C, resp.) were prepared by gas-phase grafting and their catalytic activities for MeOH oxidation were evaluated by steady-state polarization measurement. K Miyazaki, Y; Nishida, K Matsuoka, Y Iriyama, T Abe, M Matsuoka, K Kikuchi, Z Ogumi, from the Grad. Sch. of Engineering, Kyoto Univ., Katsura, Nishikyo-ku, Kyoto, Japan, *Electrochemistry* (Tokyo, Japan) 2007, **75(2)**, 217. XRD revealed that Au nanoparticles had a diameter of.approximately 4 nm and XPS revealed that Au nanoparticles deposited on Pt-Sn/C and Pt/C were in the zero-oxidation state. Electrochemical measurements performed in an aqueous solution of 1 M $HClO_4$ and 1 M MeOH demonstrated that the addition of Au nanoparticles to the Pt-Sn/C catalyst gave higher catalytic activities for MeOH oxidation than Pt-Sn/C catalyst without

Au nanoparticles. However, nano-Au/Pt/C and Pt/C showed almost identical catalytic activities.The catalytic activities of Au nanoparticles were influenced by the supporting material.

2.4 Electroactalytic Properties of Gold Nanoparticles in Oxidation Reactions of Reducting Agents

The glassy carbon electrodes modified by Au nanoparticles (200-900 ng cm-2 Au) from colloid solutions formed by Au(III) reduction with Sn(II) were found to be electrocatalysts for hydrazine, borohydride and dimethylamine borane (DMAB) oxidation in alk. solutions L Tamasiunaite, R Tarozaite, A Vaskelis from the Institute of Chemistry, Vilnius, LT-01108, Lithuania, *Chemija* 2006, **17(4)**, 13. The activity of Au particles formed in acidic and alk. solutions does not differ significantly, except hydrazine oxidation when particles prepared in an acidic medium are more active. The presence of SnO_2 (40-70 mol%) does not diminish the catalytic activity of Au particles or even enhances it. The GC electrode becomes electrocatalytically active after immersion in Au(III) solution due to a spontaneous metallic Au formation in gold ions interacting with carbon.

2.5 Rational Design of Gold Catalysts with Enhanced Thermal Stability: Post Modification Of Au/TiO_2 by Amorphous SiO_2 Decoration

Au/TiO_2 is highly active for CO oxidation, but it often suffers from sintering in high-temperature environments. In this work, The authors report on a novel design of gold catalysts, in which pre-formed Au/TiO_2 catalysts were post decorated by amorphous SiO_2 to suppress the agglomeration of gold particles. H Zhu, Z Ma, S Overbury, S Dai, Sheng from the Chemical Sciences Division and Center for Nanophase Materials Sciences,Oak Ridge National Laboratory, Oak Ridge, TN, 37831, USA, *Catalysis Letters* 2007, **116(3-4)**, 128. Even after being aged in O_2-He at 700 degree C, the SiO_2-decorated Au/TiO_2 was still active for CO oxidation at ambient temperature.

2.6 New Gold and Silver-Gold Catalysts in the Shape of Sponges and Sieves

Gold with a nanoporous sponge-like morphology, generated by leaching of AuAg alloys is presented as a new unsupported material system for catalytic applications. B Juergens, C Kuebel, C Schulz, T Nowitzki,V; Zielasek, J Biener,M Biener, A Hamza, M Baeumer, from the Institute of Applied and Physical Chemistry, University of Bremen, Bremen, 28359, Germany, *Gold Bulletin* (*London, United Kingdom*) 2007, **40**(2), 142. The role of residual silver for catalytic activity towards CO oxidation in the temperature range from -20.degree. to 50.degree. has been investigated by comparison with Au and Au/Ag zeolite catalysts. As revealed by a systematic variation of the silver content in the zeolite catalysts, bimetallic systems exhibit a significantly higher activity than pure gold, probably due to activation/dissociation of molecular oxygen by silver. By STEM tomog. we can unambiguously prove that at least some of the particles form inside the zeolite lattice.

2.7 Synthesis of Porous .alpha.-Fe_2O_3 Nanorods and Deposition of Very Small Gold Particles in the Pores for Catalytic Oxidation of CO

FeO(OH) nanorods were prepared by a mild hydrothermal synthesis using tetraethylammonium hydroxide (TEAOH) as the structure director. Z Zhong, J Ho, J Teo, S Shen, A Gedankenfrom the Institute of Chemical and Engineering Sciences, Jurong Island, 627833, Singapore, *Chemistry of Materials* 2007, **19(19)**, 4776. The as-prepared FeO(OH) was converted to porous .alpha.-Fe_2O_3 nanorods via calcination at 300 .degree.C. The .alpha.-Fe_2O_3 nanorods have a pore size distribution in the range of 1-5 nm, which is ideal to house very small gold (Au) particles. Later, by employing our invented Au- colloid-method, in which lysine was used as the capping reagent and sonication was employed to facilitate the deposition of the Au particles, we inserted very small Au particles into these pores. The prepared Au/.alpha.-Fe_2O_3- nanorod catalyst exhibited higher catalytic activity than the Au/.alpha.-Fe_2O_3 (Fluka) catalyst.

2.8 Gold Supported on a Biopolymer (Chitosan) Catalyzes the Regioselective Hydroamination of Alkynes

Gold nanoparticles on a polysaccharide-based support (chitosan) were found to catalyze with very high yields the regioselective hydroamination of terminal alkynes without the need for acid promoters and inert atm. A Corma, P Concepcion, I Dominguez, V Forne, M J Sabater, Instituto de Tecnologia Quimica UPV-CSIC, Universidad Politecnica de Valencia, Valencia, 46022, Spain, *Journal of Catalysis* (2007), 251(1), 39. The metal-support interactions were studied by Raman, IR, UV, and NMR spectroscopy. The interaction between gold and the NH and OH groups of chitosan allow good dispersion of the nanocrystals on the biopolymer. The chitosan-silica composite further stabilizes gold nanoparticles against agglomeration or leaching compared with other supports.

2.9 Hydrogen Interaction with a Ceria-Zirconia Supported Gold Catalyst. Influence of CO Co-adsorption and Pretreatment Conditions

This work reports on the hydrogen interaction with a 3 wt % Au/Ce0.62Zr0.38O2 (Au/CZ) catalyst prepared by deposition-pptn. S E Collins, J M Cies,.E del Rio, M Lopez-Haro, S Trasobares, J J Calvino, J M Pintado, S Bernal from the Departamento de Ciencia de los Materiales, Ingenieria Metalurgica y Quimica Inorganica, Facultad de Ciencias, Universidad de Cadiz, Puerto Real, E-11510, Spain, *Journal of Physical Chemistry* C 2007, **111(39)**, 14371. As deduced from X-ray powder diffraction, electron microscopy (scanning transmission electron microscopy-high-angle angular dark field and high-resolution electron microscopy), and CO volumetric/Fourier transform IR (FTIR) adsorption studies, the investigated catalyst shows a good metal dispersion.

By combining FTIR spectroscopy and volumetric chemisorption studies, it is shown that upon treating the Au/CZ catalyst with 40 Torr of H_2 at room temperature a fast and very intense spillover effect occurs. As detected from the recorded isotherm, very high values of the apparent H/Au ratio (>8.0) and of the at. hydrogen surface d. (>11.0 H/nm2) are reached. In parallel with this observation, the onset of a characteristic IR band at 2133 cm-1 shows the occurrence of significant support reduction with inherent appearance of Ce^{3}+ species.

Moreover, the simultaneous growth of the IR band at 1630 cm-1 due to mol. water strongly suggests that even at room temperature oxygen vacancies are also formed. Additional FTIR spectroscopy studies have shown that the hydrogen spillover is strongly inhibited by either co-adsorption of CO or a reducing pretreatment with flowing 5% H_2/Ar at 673 K. These deactivation effects, however, may be reverted by very mild regeneration treatments at room temperature.

2.10 Influence of the Size of Gold Nanoparticles Deposited on TiO_2 upon the Photocatalytic Destruction of Oxalic Acid

The commercially available TiO_2-photocatalyst (Degussa P25) was modified with nanosized gold particles by the photoreduction method at four different values of the pH factor of the medium. The characterization of the synthesized catalysts was carried out by the BET method, XPS, TEM and the adsorption of the model pollutant. V Iliev, D Tomova, L Bilyarska, G Tyuliev, Institute of Catalysis, Bulgarian Academy of Sciences, Sofia, 1113, Bulgaria *Journal of Molecular Catalysis A: Chemical* 2007, **263(1-2)**, 32. A remarkable influence of the pH on the particle size of Au was registered upon investigating the catalysts by XPS and TEM methods. The size of the gold nanoparticles on the TiO_2 surface decreases with increase in the pH of the medium.

The degradation of oxalic acid has been studied in aqueous solution photocatalyzed by band-gap-irradiated TiO_2, modified with nanosized gold particles. The photocatalytic activity of TiO_2, modified with gold, was found to increase with the decrease of the size of the gold nanoparticles on the surface of the photocatalytic material. The maximal value of the photocatalytic activity (twice higher than that of the semiconducting support) is registered in the case of gold photoreduction at pH 7. The adsorption properties of the catalysts, as well as the size of the noble metal nanoparticles on the surface of the support, influence the efficiency of the photocatalytic process. The reaction rate of photocatalytic degradation of the oxalic acid follows a zero kinetic order according to the Langmuir-Hinshelwood model. The increase of the quantum yield of the photodestruction reaction of the studied model pollutant is due to the formation of Schottky barriers on the metal-semiconductor interface, which serve as efficient electron traps, preventing the electron-hole recombination.

3 Chemistry

3.1 Gold(III) Reduction In A Tris-Hcl Buffer: Effect Of Riboflavin, Rutin, 1,1-Dipyridyl, and 1-Naphthol

Reduction of chloroauric acid on platinum and gold electrodes in a 0.1 M tris-HCl buffer of pH 8 containing riboflavin, rutin, 1,1-dipyridyl, or 1-naphthol is studied by cyclic voltammetry and in situ ESR methods. On the basis of the obtained data it is assumed that in the buffer there occurs the reduction of Au(III) to Au(I). S. I. Kulakovskaya, L. A Levchenko, A. V. Kulikov, A. P Sadkov, A. F. Shestakov, D. A Pichugina,from the Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow Oblast, 142432, *Russia, Russian Journal of Electrochemistry* 2007, **43(1)**, 92. In the presence of 1,1-dipyridyl, there occurs the reduction of complex [Au(III)-1,1-dipyridyl]. The reduction of Au(III) in the presence of 1-naphthol is realized in the composition of complex [Au(III)-tris-1-naphthol].

The hampering of the electrode process of the Au(III) reduction in the presence of 1-naphthol is caused by the adsorption of the [tris-1-naphthol] assocs. at the electrode surface. The presence of Au(III) does not exert any influence on the process of electroreduction of riboflavin. The obtained results make it possible to presume that the resistance of gold-accumulating cells Micrococcus luteus toward toxic compounds that are inhibitors of the respiratory chain, such as 1,1-dipyridyl and 1-naphthol, is caused by their binding in gold-containing complexes in the composition of Au-protein.

3.2 Influence of Gold Particle Size on the Aqueous-Phase Oxidation of Carbon Monoxide and Glycerol

Carbon-supported Au particles with mean sizes ranging from 5 to 42 nm and unsupported Au powder were evaluated as catalysts in the aqueous -phase oxidation of CO and glycerol. W C Ketchie,Y-L Fang, M S Wong, M Murayama, R J Davis from the Department of Chemical Engineering, University of Virginia, Charlottesville, VA, 22904-4741, USA, *Journal of Catalysis* 2007, **250(1)**, 94. For the aqueous -phase oxidation of CO at pH 14 and 300 K, the turnover frequency (TOF) for the 5-nm Au particles was 5 s-1, whereas the TOF for large supported Au (42 nm) and bulk Au were only 0.5 and 0.4 s-1, resp. The observedrate of peroxide formation during CO oxidation also was much higher on the small Au particles. Oxidation of glycerol in the aqueous phase at 333 K and elevated pH over the same catalysts revealed a similar influence of particle size, with the 5-nm Au particles giving a TOF of 17 s-1 at pH 13.8 and the larger particles and bulk Au nearly an order of magnitude less active. However, large Au particles (>20 nm) were more selective to glyceric acid. The lower selectivity of small Au particles is attributed to a higher formation rate of H_2O_2 during glycerol oxidation, because peroxide promotes C-C cleavage reaction.

3.3 Gold Supported on Cu-Mg-Al And Cu-Ce Mixed Oxides: an In Situ Xanes Study on the State of Au During Aerobic Alcohol Oxidation

Liq.-phase in situ XANES experiments were used to elucidate the oxidation state of differently supported Au catalysts during the selective oxidation of 1-phenylethanol with mol. oxygen. P Haider,J-D Grunwaldt, R Seidel, A Baiker, Department of Chemistry and Applied Biosciences, Institute for Chemical and Bioengineering, HCI, ETH Zuerich, Hoenggerberg, Zurich, CH-8093, Switz. *Journal of Catalysis* 2007, **250(2)**, 313. The catalysts include (i) Au(0.6%)/Cu3Mg3Al$_2$Ox, (ii) Au(0.6%)/Mg3AlOx, (iii) Au(2.9%)/CeO$_2$, and (iv) a copper-doped analog, Au(0.6%)/CuO-CeO$_2$ (20% CuO). The XANES and EXAFS data were collected mainly in the fluorescence mode. Simultaneous detection of the structure (XANES) and the activity of the catalysts in the continuous-flow microreactor was achieved by monitoring the oxidation state using XANES and the characteristic carbonyl vibration of the product, acetophenone, using an IR spectrometer equipped with a transmission cell.

The Au/Cu3Mg3Al$_2$Ox catalyst showed a small increase of conversion with time on stream accompanied by a slight decrease of Au content. For Au/Mg3AlOx and Au/CuO-CeO$_2$, a decrease accompanied by increased catalytic activity were observed The metallic Au is the main active species in catalytic aerobic alc. oxidation In contrast, a decrease in product formation rate was observedfor Au/CeO$_2$ with ongoing reduction. Results obtained from factor analysis indicate that the decrease in activity of the Au/CeO$_2$ with time on stream does not correlate with the much faster reduction of the catalyst and thus cannot be attributed to the increasing fraction of Au0 species. This finding corroborates the importance of recording XANES spectra for structural identification simultaneously with online detection of the catalytic performance.

4 Electrochemistry

4.1 Chronoamperometric and Voltammetric Characterization of Gold Ultramicroelectrode Arrays

Some prototypes of photolithog.-built arrays of gold ultramicroelectrodes (UMEAs) have been Electrochemical characterized and compared with a normal-size electrode. O Gonzalez-Garcia, C Arino, J M Diaz-Cruz, M Esteban from the Department de Quimica Analitica, Facultat de Quimica, Universitat de Barcelona (UB), Barcelona, E-08028, Spain, *Electroanalysis* 2007, **19(4)**, 429. The achievement of steady-state conditions, effects of supporting electrolyte and the role of conditioning and activation have been considered. The results obtained show that it is possible to monitor the effective area of those devices by chronoamperometry, which confirms the convenience of using the internal auxiliary and ref. electrodes and this evidences that steady-state currents are holding in a wide range of scan rates. Additionally, some preliminary tests show the promising features of gold UMEAs in flow systems like FIA or HPLC.

4.2 Acid Gold Plating and Palladium Nickel in Electronic Applications - An Update

A review. S J Hemsley, P Hong, Y L Chack from the Head of Research and Development (Plating), Metalor Technologies Pte Ltd., Singapore, 638074, Singapore, *Proceedings – AESF SUR/FIN Annual International Technical Conference* 2006 547. This paper will provide a technol. update on the state of the art processes for both Palladium Nickel and Acid Gold, it will explore the tech. aspects and also the financial implications as a result of changing metal prices. Data will be presented giving performance data on Porosity, Contact Resistance and Corrosion related to thickness reduction. Newly developed processes will be highlighted and their features and benefits explored. New applications and trends in Connector, Semi Conductor Lead Frame and Microelectronics will presented.

5 Electronics and Sensors

5.1 Fabrication of Nanoporous Gold Film Electrodes with Ultrahigh Surface Area and Electrochemical Activity

Nanoporous Au film (NPGF) electrode was fabricated by applying multicyclic potential scans on a polished Au electrode in an electrolyte composed of ZnCl$_2$ and benzyl alc. F Jia; C Yu; Z Ai; L Zhang, from the Key Laboratory of Pesticide Chemical Biology of Ministry of Education, College of Chemistry, Central China Normal University, Wuhan, 430079, Peop. Rep. China, *Chemistry of Materials*, 2007, **19(15)**, 3648. In the cathodic potential scan, Zn was 1st electrodeposited on the Au electrode surface, and Au-Zn alloy was then directly formed on the surface under an elevated temperature In the subsequent anodic potential scan, dealloying of Zn took place, resulting in a nanostructured Au film. Also, Zn was then electrodeposited onto the porous Au surface and a Au-Zn alloy was formed at the same time.

Through controlling the parameters of cyclic voltammetry and cyclic times, the authors finally obtained a 3-dimensional NPGF with nanopores. The resulting NPGF possessed ultrahigh roughness factor and surface area. The Electrochemical activity of the NPGF electrode was much higher than that of the polished Au electrode. Probably the resulting NPGF electrode is promising in the fields of catalysis, sensors. Meanwhile, this multicyclic Electrochemical alloying/dealloying method may be applied to fabricate other nanoporous metal films.

5.2 The Effect of Silica Coating on the Optical Response of Sub-Micrometer Gold Spheres

The effects derived from the growth of SiO2 shells on the optical properties of sub-micrometer Au spheres were studied as a function of shell thickness. J Rodriguez-Fernandez; I Pastoriza-Santos;J Perez-Juste,F Garcia de Abajo,L Liz-Marzan

from the Departamento de Quimica Fisica and Unidad Asociada CSIC, Universidade de Vigo, Vigo, 36310, Spain, *Journal of Physical Chemistry C*, 2007, **111(36)**, 13361. The dipole plasmon resonance mode of these large spheres is significantly more sensitive to changes in the medium refractive index than the quadrupolar mode, in agreement with theor. modeling based on the boundary element method (BEM) for concentric spheres. Near-field maps of both resonance modes in such coated nanoparticles show that the areas with significant near-field enhancement get progressively located within the SiO_2 shell as its thickness increases, with basically no enhancement outside of the shell when this is thicker than the sphere radius.

5.3 Gold-Nanoparticle-Doped TiO_2 Semiconductor Thin Films: Optical Characterization

A simple procedure for creating titania sol-gel-based semiconductor thin films is described. D Buso, J Pacifico, A Martucci, P Mulvaney, School of Chemistry, University of Melbourne, Parkville, VIC, 3010, Australia, *Advanced Functional Materials*, 2007, **17(3)**, 347. Gold nanoparticles are doped homogeneously into the precursor mixt. and the particles are homogeneously distributed in the resultant films when prepared using spin-coating. The effects of particle loading and annealing temperature on the optical properties of the resultant films were characterized. Ellipsometry, x-ray diffraction, at. force microscopy, and surface plasmon spectroscopy were used to monitor the crystn. and porosity changes during film synthesis.

6 Medical and Dental

6.1 Playaz Dental Grillz, Dental fixtures comprising Surgical Metals,

Playaz dental grillz are dental fixtures that enable a custom fit without the need of user molding. The use of surgical metals, silicon padding, UV coating and a unique 4 prong attachment enable this safely. The use of 24K gold or rhodium plating and cubic zirconium provide a jewelry image and it is being marketed as a temporary fashion look. H Y Kim, Patent No US 2007264614, A1, November 2007.

7 Metallurgy, Materials and Coatings

7.1 Determination of Gold and Silver in Copper Matte by Fire Assay

High contents of gold and silver in copper matte were detected by fire assay. The method was high in accuracy and good in precision. H-Y Wang, D-X Yin, D-Y Cong, Beijing General Research Institute of Mining and Metallurgy, Beijing, Peop. Rep. China, *Kuangye (Beijing, China)*,2006, **15(Suppl.)**, 45. The percentage recovery was between 99-102%. The method met detection demand of gold and silver in copper matte.

7.2 Chrysotype: Photography in Nanoparticle Gold

A review. M Ware, Buxton, SK17 6HH, UK, *Gold Bulletin (London, United Kingdom)* 2006, **39**(3), 124. The printing of photographs in pure gold, rather than the ubiquitous medium of silver, was first achieved in 1842 by Sir John Herschel, but his innovative 'chrysotype' process was soon consigned to obscurity, owing to its expense and uncertain chem. In the 1980s some modern coordination chem. of gold was applied to overcome the inherent problems, enabling an economic, controllable gold-printing process of high quality, which offers unique benefits for specialised artistic and archival photog. purposes. The color of the gold image depends on the dimensions of the nanoparticles, which are controlled by the parameters of the photochemical process.

7.3 Fabrication of Gold Nanowires by Electric-Field-Induced Scanning Probe Lithography and in-Situ Chemical Development

Sowing seeds to grow nanowires is an approach for the fabrication of surface-confined gold nanostructures for electronic and plasmonic applications. W-K Lee, S Chen, A Chilkoti, S Zauscher, Department of Mechanical Engineering and Materials Science, Duke University, Durham, NC, 27708, USA, *Small* 2007, **3(2)**, 249. Clusters of gold atoms (seeds) are deposited during nanostructure patterning by elec.-field-induced scanning probe nanolithography, and these seeds are subsequently developed in-situ. This simple approach can be extended to other metals and is promising for massively parallel implementation through anodization stamping.

8 Nanotechnology

8.1 Intrinsic Reactivity of Gold Nanoparticles: Classical, Semi-Empirical and DFT Studies

Gold nanoparticles used in most experiments (1-10 nm) in gold catalysis show varying degrees of reactivity, with particles below 5 nm generally being more reactive. N S Phala, E van Steen. Technology Department, Anglo Research, Crown Mines, 2025, S. Africa, *Gold Bulletin (London, United Kingdom)* 2007, **40(2)**, 150. The origin of this activity is a subject of a no. of model experiments and theor. studies on either clusters of a few atoms in size of extended surfaces (smooth or stepped). In the work described here, a classical theory for the variation of the metal workfunction with cluster size,

Extended Huckel Theory (EHT) calcns. combined with DFT calculations, as well as a carbon monoxide (CO) chemisorption model are combined to develop a relationship between metal particle size and the particle's reactivity towards CO. For gold, it is shown that while the contribution of the d-band hybridization energy to the total CO chemisorption energy is unfavorable for bulk gold, this is not true for gold particles below 5-6 nm. That is, the d-band hybridization energy is neg. for small gold particles. This is believed to be explanation of the onset of high reactivity for small gold particles.

8.2 Synthesis of One-Dimension Nano Gold Materials by Sol-Gel Template Method

The synthesis of one-dimension nano Au materials by sol-gel template method was studied. Highly ordered one-dimension nano Au materials were prepared from HAuCl4 and trisodium citrate solution with the porous anodic G Shao; X Zhang;B Liu;Y Huang,Z; Du, Key Laboratory for Special Functional Materials, Henan University, Kaifeng, 475001, Peop. Rep. China, *Xiandai Huagong* 2006, **26(1)**, 44. Al_2O_3 as templates based on a sol-gel method. Au nanotubes and nanowires could be obtained by controlling the concentration of the Au sol and the immersing time of the template in the sol. The morphology and structure of the gold materials were characterized by SEM, TEM, SAED and XRD: their diameter was about 200 nm, and the length could be up to several dozens of nanometers. The formation mechanism of the 1D gold nanomaterials was discussed briefly.

8.3 Seed-Mediated Growth of Uniform Gold Nanoparticle Arrays

The authors demonstrated through electron microscopic characterizations that the semi-hexagonal Au nanoparticle arrays supported on solid surfaces prepared by a polymer template approach could be enlarged uniformly by using a solution-based seed-mediated growth. S Kumar, H Yang, S Zou, Department of Chemistry and Biochemistry, Miami University, Oxford, OH, 45056, USA, *Journal of Physical Chemistry C* 2007, **111(35)**, 12933. The semi-hexagonal particle arrangement is largely retained after the growth as evident by the similar Fourier transform patterns obtained before and after the growth, indicating that the growth occurs over the seed particles on the surface. The shape and size of the augmented particles can be tuned by varying the growth conditions. The particle d. can be conveniently varied by using polymer templates with different chain lengths. The growth mechanism is briefly discussed. Strong surface-enhanced Raman signals of mols. adsorbed on the 40-60 nm grown particles are observed.

8.4 Shape-Controlled Synthesis of Highly Monodisperse and Small Size Gold Nanoparticles

Fine control of nanoparticle shape and size can be achieved by systematic variation of experimental. parameters in the seeded growth procedure in aqueous solution Y Fu,Y Du; P Yang; J Li;L Jiang, Department of Chemistry, Suzhou University, Suzhou, 215006, Peop. Rep. China, *Science in China, Series B: Chemistry* 2007, **50(4)**, 494. Cubic and spherical gold nanoparticles were obtained, resp. In particularly, the Au cubes were highly monodisperse in 33 nm diameter The experimental. methods involve the preparation of Au seed particles and the subsequent addition of an appropriate quantity of Au seed solution to the aqueous growth solutions containing desired quantities of CTAB and ascorbic acid (AA).

Here, AA is a weak reducing agent and CTAB is not only a stable agent for nanoparticles but also an inductive agent for leading increase in the face of nanoparticle. UV visible spectroscopy, x-ray diffraction, and TEM were used to characterize the nanoparticles. The different size gold nanoparticles displayed high size homogeneous distribution and formed mono-membrane at the air/solid interface.

8.5 Fine-Tuning Size of Gold Nanoparticles by Cooling during Reverse Micelle Synthesis

By lowering the reaction temperature during metal ion reduction in a reverse micelle system, gold nanoparticle size can be subtly tuned from 6.6 to 2.2 nm in diameter Under these reaction conditions, the water-to-surfactant ratio (W value) also plays an important role in controlling the particle size, enabling a wide range of products obtainable via a simple, quick, reproducible synthesis. Particle sizes were measured by HRTEM, and size trends were supported by UV-vis spectroscopy. A B Smetana, J S Wang, J Boeckl, G J Brown, C M Wai,Department of Chemistry, University of Idaho, Moscow, ID, 83844-2343, USA, *Langmuir* 2007, **23(21)**, 10429

8.6 Photochemical Synthesis and the Seeding-Mediated Growth of Gold Nanoparticles under the Sunlight Radiation

In the aqueous citrate-chloroauric acid soln., well-dispersed gold nanoparticles were synthesized by the photochem. reduction under the UV solar radiation on plateau. H Wu, S Dong, Y Dong, C Tang, S Yang, Kunming Inst. Precious Metals, Kunming, 650221, Peop. Rep. China, *Gaodeng Xuexiao Huaxue Xuebao* 2007, **28(1)**, 10. The influences of the pH of the mixt. solution and the UV solar radiation conditions on the photochem. reaction rate and the size of gold nanoparticles were investigated. By means of seeding-mediated growth approach, monodispersed spherical gold nanoparticles with an average diameter from 4.9 nm to 9.7 nm and with a narrow size distribution were obtained by varying the ratio of Au(O) seed to Au(III) ion under suitable conditions. Based on the characterization by UV-Vis adsorption spectrum and transmission electron microscope (TEM), the mechanisms of the freedom radical reaction, the nucleation and growth during the formation process of the gold particles were discussed.

9 Refining

9.1 Gold Recovering Equipment Capable of Improving Recovery Efficiency of Gold Contained in a Plating Solution or Aqua Regia

A gold recovering equipment that improves recovery efficiency of gold by using a first filter, a second filter and a third pipe and prevents backflowing of the solution within the container through a first pipe by opening or closing a second pipe according to a level of a plating solution contained in a container is provided. An equipment for recovering gold comprises: a container having a first pipe connected to an upper portion thereof and a second pipe connected to a

lower portion thereof; a first filter which is installed within the container at a first elevation identical to an elevation to which the second pipe is connected so as to cut out the second pipe, and which adsorb gold contained in a solution supplied through the first pipe; a level sensor for measuring a level of the solution contained in the container; and a drive part for moving the first filter to open the second pipe if an elevation of the solution is a preset elevation or higher as measurement results of the level sensor, and moving the first filter to cut off the second pipe if the elevation of the solution is lower than the preset elevation. J Lee, Y Lim, Y Kim from the Samsung Electronics Co., Ltd., S. Korea, Patent No. KR 2007001511, A, April 2007

9.2 Keto Sulfides Derived from Tert-Dodecyl Mercaptan and their Extractive Power with Respect to Palladium(II) and Gold(III)

Gamma.-Keto sulfide concs. were prepared by alkylthiomethylation of propanone, butanone, and acetophenone with tech.-grade tert-dodecyl mercaptan and other sulfur-contg. substances, and their extractive power with respect to palladium(II) and gold(III) from hydrochloric acid solutions (chloroform as diluent) was studied. A. N. Kalimgulova, M. A. Parfenova, A. D. Ulendeeva, N. K. Lyapina, R. A. Khisamutdinov, Y I Murinov, Institute of Organic Chemistry, Ufa Scientific Center, Russian Academy of Sciences, Ufa, Bashkortostan, Russia, *Russian Journal of Applied Chemistry* (2006), 79(11), 1798

9.3 The Effect of Sulphur Species on Thiosulphate Leaching of Gold

Thiosulfate is a metastable anion that tends to readily undergo chem. decomposition in aqueous solutions D Feng, J S J van Deventer, Department of Chemical and Biomolecular Engineering, The University of Melbourne, Parkville, 3010, Australia, *Minerals Engineering* 2007, **20(3)**, 273. The presence of tetrathionate, trithionate, and sulfide is unavoidable in the ammoniacal thiosulfate system, as they are products of thiosulfate decomposition Thiosulfate decomposition is of great importance in the thiosulfate leaching of gold. The effect of three typical sulfur species tetrathionate, trithionate, and sulfide on thiosulfate leaching has been investigated in both pure gold and ore systems. The gold dissolution increased at low concns. of the sulfur species, but decreased at high concns. The presence of these sulfur species significantly reduced thiosulfate decompn., and this beneficial effect became more prominent at high levels of the species.

The Eh-pH diagram for the Au-N-S-H_2O system indicated that the sulfide ion could form HS- to complex gold, enhancing gold leaching. Tetrathionate, trithionate, and sulfide would convert to thiosulfate with some elemental sulfur being formed via oxidation or reduction routes. The presence of the sulfur species shifted the thiosulfate decomposition reactions, and hence stabilized thiosulfate. Raman spectra demonstrated that the gold surfaces were readily passivated in the presence of the sulfur species, and the passivation tended to be more severe at higher levels of the species.

9.4 Evaluation of Kinetic and Diffusion Phenomena in Cyanide Leaching of Crushed and Run-of-Mine Gold Ores

This paper compares the rates of pore diffusion and cyanide gold dissolution in coarse, porous gold oxide ore particles. S C Bouffard, D G Dixon, Barrick Technology Centre, Vancouver, BC, V6A 1C4, Can.*Hydrometallurgy* 2007, **86(1-2)**, 63. Several size fractions of a gold oxide ore from a Nevada heap leaching operation were leached individually in a well mixed solution of const. pH (10.5, 11, or 12), const. cyanide concentration (50, 200, or 500 ppm), and const. temperature (5, 22, or 40 .degree.C). Particles were coarse, ranging from - 1.7 mm (10 mesh) to 152 mm (6 in.). Leaching of -1.7 mm (10 mesh) particles was complete in 24 h. The leaching kinetics was not influenced by the pH or the dissolved gold concentration.

A model, which does not include the pore diffusion, as the latter was found to be extremely rapid in such small particles, predicts the conversion X as a function of time, cyanide concentration and temperature According to the data and the model, increasing temps and increasing cyanide concns were found to increase the leaching kinetics. Leaching of larger particles was much slower than -1.7 mm (10 mesh) fines, requiring as many as 85 days to reach near complete gold extraction from particles 102 mm (4 in.) to 152 mm (6 in.) in size. In a static cyanide heap leach operation, this time period is very comparable to the time of irrigation of the uppermost lift.

According to the diffusion/reaction model developed for the coarse particles, the advance of cyanide and oxygen into the pores of these particles was found to be slower than in the -1.7 mm (10 mesh) particles, but still was much faster than the gold dissolution reaction itself. The outward diffusion of dissolved gold was also found to be very rapid. The precise measurements of the gold dissolution kinetics of coarse particles made in this study dispels, in part, the well-accepted hypothesis that solute diffusion rates control gold heap leaching of crushed and run-of-mine ores. The kinetic model that we have developed for coarse ore leaching in well mixed environments could also predict accurately the gold extraction in large columns. This evidence attests to the slowness of the dissolution of gold in coarse particles, unfortunately leaving crushing alone as the most effective option to shorten the leach cycle.

10 General

10.1 How Gold Drops Drill Holes - Corrosion Emergence of Refractory Bricks in Glass-Melting Furnaces

The damaging effect of agglomerating gold clusters (some hundred .mu.m to some cm) if melting ruby colored glass

on glass-furnace linings is studied being the result of a local Marangoni-driven convection flow generated by the differences of surface tension of lining material and glass at one hand and molten glass and gold melt on the other hand.

M Thoennissen, R Telle, Lehrstuhl fuer Keramik und Feuerfeste Werkstoffe, Institut fuer Gesteinshuettenkunde, RWTH, Aachen, D-52064, Germany, *Sonderbaende der Praktischen Metallographie* 2006, **38**, 495